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September 13, 1991

Dr. Larry Cooper
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Dear Larry,

Please find enclosed summary of my work in various areas, carried out under the auspices of your electronics program. Work so far falls into a number of groups: (1) continuation of the Schottky barrier studies; (2) work on early stages of Schottky barrier formation (with John Klepeis; (3) work on properties of SiC with Walter Lambrecht and Ben Segall at Case; (4) general development of the methods, most particularly the "ultimate electronic structure program" that I've design together with Michael Methfessel in Berlin; (5) "current projects," and plans for the near future.

Work on parts (1-3) have been completed, though more work is in progress. John Klepeis is just now writing up some very nice results on part (2) in two papers. The papers will not be complete for another two or three weeks, so I took the liberty of waiting for the finished versions of the papers, rather than send you partially completed draft copies. As soon as they are ready for submission, I'll be sure to forward a copy to your office. The main conclusions are summarized in the accompanying report.

I do hope you can fit SRI into your schedule in the next few months. It

would be nice to see you, and I look forward to the opportunity to show you "up close" what we are up to here.

Sincerely Yours,

Mark

Mark van Schilfgaarde

Statement A per telecon
Dr. Larry Cooper ONR/Code 1114
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NWW 10/3/91

September 13, 1991

This report summarizes work development and application of advanced methods in electronic structure to semiconductors. The work was carried out under the auspices of the Office of Naval Research, contract N00014-89-K-0132.

1. Schottky Barrier Studies

Two comments have appeared concerning the Schottky barrier work (see enclosed). One from F. Flores has appeared in print, and the other from J. Freeouf, J. Woodall and C. Duke is likely to be published shortly. These comments were concerned with how our detailed calculations addressed model theories that purport to explain pinning of the Schottky barrier, in particular the "neutral point, or MIGS" theory of Tejedor, Flores and later Tersoff; and the "effective work function model" of Freeouf and Woodall. Our detailed calculations showed that, owing to the large dielectric response of the interface and a high density of interface states throughout the gap, the Fermi level is constrained to lie very near the point where interface is charge–neutral. This confirms that the "neutral point" theory of Flores *is* correct on this point, that there exists a "neutral point" which pins the Fermi level, and thereby establishes unequivocally that the Schottky picture, which assumes *no* screening at the interface, is essentially irrelevant to the Schottky barrier. However, the "neutral point" picture was shown to be erroneous on second point, namely its *assumption* that the neutral point is a *universal* property of the semiconductor alone. Tersoff for example, hypothesizes a neutral point that is calculated from a Green's function of the *bulk* semiconductor band structure, and therefore can contain no information at all about the bonding at the interface. Our calculations show explicitly that the neutral point is very much a property of the details of the bonding at the metal-semiconductor contact. In particular we showed the metal *d* electrons can shift the neutral point throughout the bandgap. These calculations show pretty clearly that *both* the "neutral point" theory and the Schottky picture (on which the Effective Work Function model is based) are are founded on flawed assumptions, and so we rejected them.

The comments concerning these conclusions made essentially two points. Firstly, they point out that our calculations have some problems too—mainly the underestimate of the bandgap. (But this is really a side issue, because the assumptions in

either of these models should hold, if they are true, whether or not we use an approximate LDA hamiltonian or the exact many-body one. It makes no difference that our calculation solves the Schrödinger equation only for an approximate potential.) Secondly, they both noted that if one *relaxes* the interface, the barrier height may change. While this point is legitimate, it doesn't really help either the "neutral point" theory or the Schottky picture, there is still lacking an explanation that would explain how interfacial relaxation patches up the flawed assumptions in these models.

These conclusions indirectly support Prof. Spicer's "defect model," since they exposes difficulties in the main competing theories of Schottky barrier pinning. In the PCSI paper (see enclosed) we began to explore the rôle of defects near the intimate contact. We drew several important conclusions. (1) Defects near the intimate contact can strongly influence the pinning position of the Fermi level, in spite of the strong screening there. Several authors—Tersoff for example—have argued that the screening is so strong that defects will be "screened out." These explicit calculations show that this is simply not so. (2) It is not generally the defect with the *greatest number* that will generally predominate the pinning behavior; rather it is the defect *interiormost* from the intimate contact (provided there is a minimum number available to pin). (3) Defects near the intimate contact actually form a kind of extended interface region, with a continuum of states in the gap throughout the extended region. Thus only a single kind of defect is needed pin the fermi level, regardless of whether the semiconductor is n or p type. This picture is somewhat different from what Spicer offered, who thought of the defects as bulk-like, and thus needed two kinds of levels to explain pinning in both n and p type materials. Moreover, since they are still coupled to the "MIGS," they are stable on applied voltage, which explains how they still will pin the fermi level even on applied bias. These conclusions obviate one of the key difficulties associated with the defect model of fermi–level pinning.

2. Early Stages of Schottky Barrier Formation

The focus of our surface studies has been on the evolution of the electronic properties of the metal-semiconductor interface as a function of metal coverage. We have carried out first-principles electronic structure calculations for Au, Al and Cs on the GaAs (110) surface. We have considered coverages ranging from 1/8 to 5 monolayers (ML) (1 ML corresponds to the density of Ga or As surface atoms), studying three different aspects of the electronic structure: (1) the critical dependence, at low coverages, of the surface electronic structure on the charge state of the adatom, (2) the evolution with coverage of the Fermi level relative to the semiconductor bands and (3) the transition from a Mott-insulating overlayer at low coverages to a metallic overlayer at high coverages.

At sufficiently low coverages ($\leq 1/2$ ML), all of our calculations (for Au, Al and Cs)

reveal the existence of a very narrow half-filled band in the semiconductor bandgap. This band is typically composed of a linear combination of adatom-derived states and substrate-derived dangling-bond states. When the density of adatoms is small, the band is very narrow. In this low-density limit, the wavefunctions are more appropriately described in terms of a localized Mott-insulating state rather than an itinerant Bloch state. The Hubbard model provides a convenient framework for discussing the physics of this localized state. The two parameters of this model are the correlation energy U, which represents the additional electron-electron repulsion that occurs when two electrons occupy the same localized state, and the hopping integral t, which is proportional to the bandwidth, and therefore the overlap between the wavefunctions in adjacent unit cells.

In the low-density limit $t \rightarrow 0$; thus $U >> t$, and the usual band picture such as the LDA provides, is inapplicable. However, several authors have shown, in connection with the high-temperature superconductors (McMahan, Annett and Martin, 1990), that the LDA still provides useful information even in the limit when the electrons are highly correlated. In particular, the parameters U and t can be extracted from an LDA calculation. Once extracted, they can be employed in a Hubbard model to investigate the electronic structure in the low-density limit. This procedure provides a way to obtain "first-principles" model Hamiltonians. By calculating the total energy for different charge states within the LDA, we have extracted the parameters U and t for Au and Al adatoms on the GaAs (110) surface (Klepeis and van Schilfgaarde, 1991). We find that U is approximately 1 eV with t being an order of magnitude smaller for coverages up to 1/2 ML (uniformly distributed adatoms).

The second aspect of the electronic structure of metal-semiconductor interfaces that we have investigated is the evolution of the Fermi level as a function of coverage. This problem has been studied in detail using tight-binding theory (Klepeis and Harrison, 1989). Our new LDA calculations (Klepeis and van Schilfgaarde, 1991) confirm the qualitative features of this earlier work and provide quantitative values for the model parameters (e.g. the parameters U and t). In addition, the first-principles calculations provide additional insights which were not evident in the simpler tight-binding treatment: electronic charge is transferred from the adatom to the substrate, giving rise to an adatom-substrate surface dipole. As the adatom coverage is increased, the dipole-dipole interactions produce a coverage-dependent shift in the position of the Fermi level relative to the semiconductor surface bands. The LDA calculations (Klepeis and van Schilfgaarde, 1991) indicate that the origin of this adatom-substrate dipole can be much more complex than simple electronegativity arguments would indicate. In particular, the dipole as well as the position of the Fermi level in the gap are sensitive to the *atomic geometry* as well as the detailed electronic structure of the interface, which depends on the *kind* of metallic adatom. These conclusions are similar to those drawn for the bulk Schottky barrier; see above. Thus, simple "charge-neutrality point" models (Tersoff, 1984), derived solely from bulk semiconductor properties, do not properly describe the physical behavior of the

interface.

A third aspect of the electronic structure that we have investigated is the transition from an adatom-derived Mott-insulating state to a fully metallic overlayer. Our results can again be stated in the terminology of the Hubbard model. At low coverage U is much larger than t and the electronic structure is dominated by correlation effects. At coverages above 1 ML the wave functions overlap significantly and we recover the usual band picture with itinerant Bloch states. The exact coverage at which the transition occurs is of great interest (DiNardo et al., 1990 and Whitman et al., 1991). In the case of Al, one might guess that 1 ML of adatoms would be metallic, because this density is very nearly equal to the density of Al atoms at the Al (110) surface. However, by examining the charge density arising from the adatom-derived band in the gap and by comparing the bandwidth to the calculated value of U, we only find clear evidence of metallization at 2 ML but not at 1 ML (Klepeis, Mailhiot and van Schilfgaarde, 1991).

The explanation for this surprising result is that the first ML of metal is strongly bonded to the substrate. Inspection of the charge density for the band in the gap indicates that a tight-binding-like picture with directional bonds is the most appropriate description for the adatom-substrate interaction (Klepeis, Mailhiot and van Schilfgaarde, 1991). The overlap between these directional bonds in adjacent unit cells is quite small leading to a small bandwidth and a lack of metallic behavior. In this way the adatom-substrate interaction inhibits the metallization of the first ML. However, this first ML "satisfies" the substrate and so the second ML is free to form a 2-dimensional metal. This qualitative picture appears to be quite general; our calculations for Au and Cs also indicate that the substrate inhibits the metallization of the first layer of adatoms but that the second layer is metallic. Our calculations are in qualitative agreement with recent EELS (DiNardo et al., 1990) and STM (Whitman et al., 1991) experiments which addressed the question of metallization for Cs on GaAs (110). However, in order to compare directly with experiment, the atomic geometry must be allowed to relax in our calculations. In addition, model calculations are needed which adequately describe both the Mott-insulating and the metallic limits. These systems hold promise as a new experimental testing ground for two-dimensional Hubbard models.

One final, but preliminary aspect of our studies concerns the lattice dereconstructions, or attendant to the deposition of metal overlayers. As metal overlayers are deposited, partially dereconstructs to assume the lattice more closely resembling the bulk semiconductor. Some preliminary studies of these dereconstructions have led to the following conclusions. (1) The semiconductor lattice dereconstructs to about 75% of the way to the bulk material; and (2) dereconstructions are approximately independent of the metal overlayer. Cases studied were Au, Ag and Al. So far we have constrained the dereconstructions to lie somewhere between the perfect lattice and the reconstructed lattice of the free surface. In the near future, our more efficient electronic structure program will become available (Section 4). One first application

will be to complete this work, carrying out comprehensive studies of the evolution of reconstructions as metal overlayers are added.

References

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3. Studies of SiC

Two papers on studies of SiC are enclosed, which discusses work done in collaboration with Walter Lambrecht and Ben Segall at Case. The first paper has been published in the Proceedings of the MRS, concerns a study of inversion domain boundaries in SiC and GaAs. (Though SiC is composed of two column IV elements, it is really more like a III-V compound since C is much more electronegative than Si, and the bond is quite polar.) The inversion domain boundary is a boundary between domains with inverted anion and cation positions. Thus, the interface is characterized by "wrong bonds," meaning cation–cation bonds and/or anion–anion bonds. A {110} boundary of this type has equal numbers of cation–cation and anion–anion bonds; a {100} boundary has only one or the other. "Wrong bonds" are important in other grain boundaries, because many of them involve 5– and 7–fold rings. Since odd-numbered rings necessarily contain a "wrong bond," their study is important generally in the study of grain boundaries. The enclosed paper outlines a procedure for defining the energy of such grain boundary. Total–energy calculations of a number of them were performed, allowing lattice relaxations of the nuclei nearest to the interface.

The main goal of this study was to try and characterize the grain boundary in terms of "wrong bonds" that are independent of one another, much like Walter Harrison's characterization of a semiconductor in terms of independent, or nearly independent bonds. If we could succeed in simplifying the physics of the interface to independent "wrong bonds," we could apply these same ideas and gain a simple, and quite general understanding of whole classes of grain boundaries, such as the energetics of 5– and 7– fold rings.

Unfortunately, the true situation turned out to be much more subtle than that.

The energetics of a "wrong bond" were found to depend quite strongly on the local environment; thus the energy of a {110} boundary (with on Si-Si bond and one C-C bond) is quite different than the average of a {110} boundary with only Si-Si bonds and one with only C-C bonds. Some of the differences have to do with lattice relaxations, which depend on the local environment, some with electrostatic interactions (which by their very nature are "nonlocal"), and some also with the chemical interactions between "wrong bonds." To the extent that a "wrong bond" *can* be characterized as an independent entity, we was found their formation is rather costly energetically, particularly in SiC. In SiC "wrong bonds" cost roughly 50% of the Si-C bond energy, and in GaAs cost roughly 20% of the Ga-As bond energy. Thus, the grain boundary energies, (with only the simple relaxations considered) turn out to be quite large. However, because these energies change considerably with changes in environment, these numbers can become significantly lower.

3.1 MECHANICAL PROPERTIES OF SIC

A second paper, which has been accepted for publication in *Phys. Rev.* B, deals with mechanical properties of bulk SiC. Accurate values of elastic constants and deformation potentials are important for device applications of SiC. For example, in strained layer heterojunctions using SiC, the single most important quantity for device applications is the heterojunction band offset and its strain dependence, *i.e.* the deformation potential. Because much of this information is not yet available experimentally, these quantities were calculated using the FPLMTO method. Quantities calculated include the equilibrium lattice constant, the cohesive energy, the bulk modulus and its pressure derivative, the elastic constants, the zone-center transverse optical phonon frequency, its Grüneisen parameter and the corresponding energy band strain and optical mode deformation potentials. Calculated values agreed well with experimental data where it was available. Probably the most important results are the full complement of calculated deformation potentials, particularly since these are not available experimentally.

4. Electronic Structure Method

The last topic concerns development of the "ultimate electronic structure" method. This development is largely complete, but for which some development and testing is needed before the method can be used in practice. In some sense this effort is the most important, since we believe it will play a major rôle in the future course of electronic structure methods. Car and Parrinello touched off a newer generation of electronic structure methods with their "iterative diagonalization" scheme. In effect, Car and Parrinello found a more clever way to obtain eigenvalues of a Hamilto ian using a plane wave basis, exploiting special properties of plane waves. But because their approach is more efficient than conventional plane-wave approaches, it allows for

much more complex calculations than could be done previously, using the plane wave method. Michael Methfessel and I sought to build a new method that embodies all of the advantages of more efficient methods, while retaining the advances of iterative diagonalization schemes such as the Car Parrinello method. We particularly sought several properties for our method which the plane-wave methods do *not* possess: (1) that it be a real-space method, and thus amenable to applications that require such an approach, (2) that it use a small, efficient basis set, and (3) that it be applicable to any element in the periodic table.

Any full-potential method must deal with the following obstacles: (1) re-expression of wave function *products* to obtain, for example the charge density; (2) solution of the Poisson equation; (3) matrix elements of the Hamiltonian. All of these are easy with a plane wave method, because the product of two plane waves is yet another plane wave. Thus, integrals of plane waves, and products of them, are more or less trivial. Similarly, Poisson's equation is trivial because plane waves are eigenfunctions of them. For most functions, these requirements are not usually feasible.

We chose as our basis the usual LMTO's, because they are known to be the most efficient, most "intelligent" basis set available. It major drawback concerns requirement (1). The products of two LMTO's cannot analytically be re-expressed in terms of anything simple. Our solution was to generate a lookup table that re-expressed the product of two LMTO's, centered on sites A and B respectively (see Fig. 1), as a sum of "smoothed Hankel functions" centered on the same sites. This cannot be done analytically, but we do it as carefully and as accurately as we like with a least-squares fit, once and for all, and then put it into a "lookup table." To show that this method really works, Fig. 1 shows a contour plot of the product of two LMTO's centered on separate sites, and its re-expression into combinations of smoothed Hankels. It turns out that "smoothed Hankel functions" are also essentially eigenfunctions of Poisson's equation; and also matrix elements of the Hamiltonian are equally easy. Thus, the other key barriers to the method are easily solved.

It turns out that there are many practical details that make this method far more complicated that a pseudopotential or LAPW program, and it has taken some significant effort to make it all work. However, the potential for large gains in efficiency is quite evident, and we are optimistic that the effort expended will be well worth it. We have just completed the "molecules" version of the program. Figure 2 shows the charge density of an N_2 molecule calculated self-consistently. It takes only about 30 seconds to complete this calculation on our workstation. We are presently in the process of converting it to a "solids" program—this is not a particularly difficult task.

To compare the power of this method with other methods, consider that today *all* methods suffer from an essential limitation on system size: the computation time for all methods increases as the third power of the number of atoms N in the systems. Thus, while the Car-Parrinello method is much more efficient than its predecessors, it quickly bumps up against this so-called N^3 problem. But because our method is a real-space method, it turns out that operation of Hamiltonian on trial eigenvectors

scale as the *square* of the number of atoms N for moderate and large systems. This is an enormous improvement, and we should be able to accomplish this in the near future. Moreover, for very large systems, other techniques can be used which are amenable only to real-space methods. In particular, the recursion method requires a real-space method, but the computational effort for that method scales only *linearly* with N.

5. Work in Progress

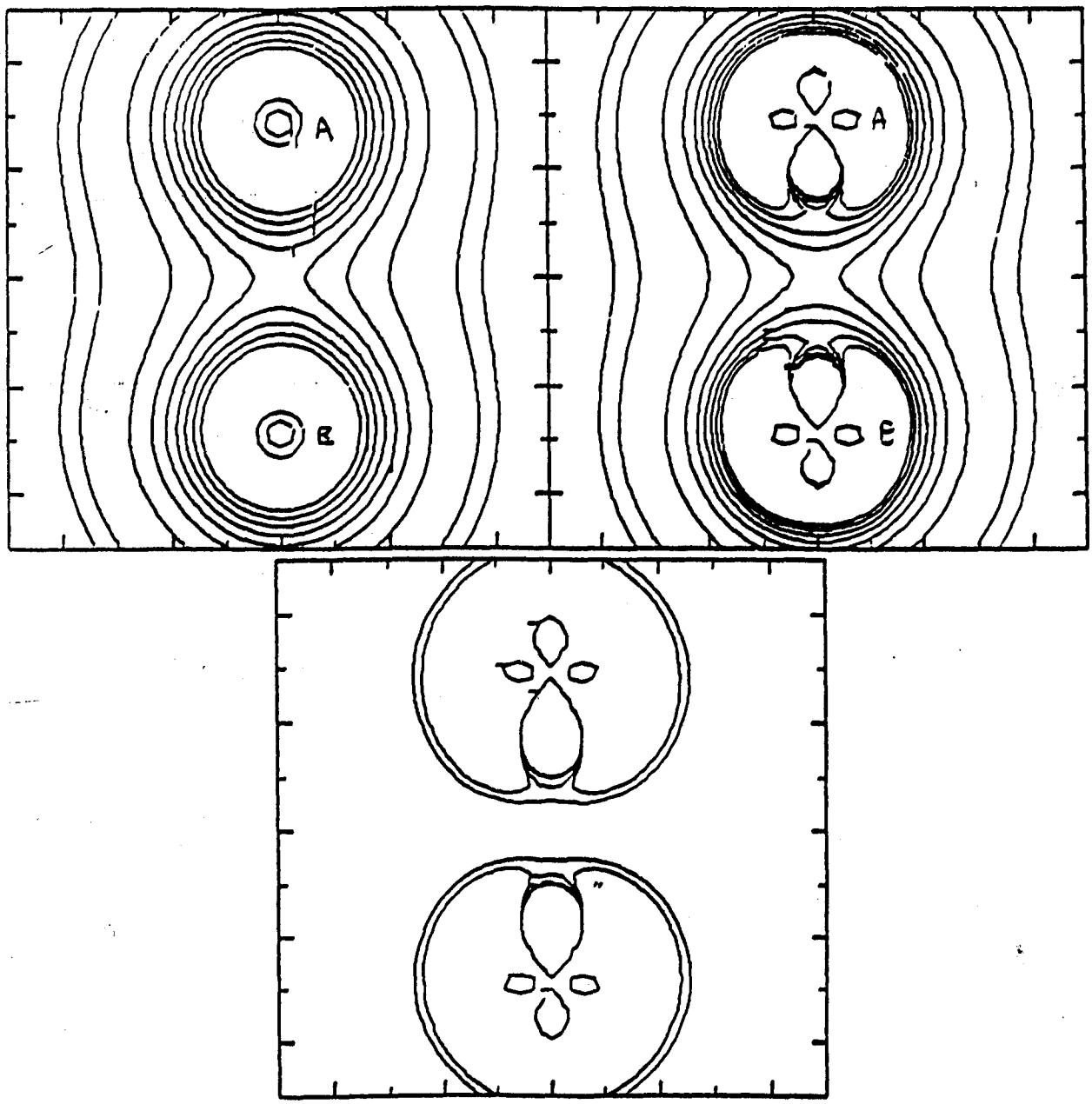
Another project now in progress in collaboration with Marcy Berding here at SRI, concerns defect formation energies in ZnTe, CdTe and HgTe, in particular the antisite defects and vacancies. We have completed preliminary calculations of both kinds of defects in CdTe and HgTe, with some limited relaxation of neighboring atoms. One of the more interesting conclusions we have drawn is that Te antisite energy is calculated to be significantly *lower* in CdTe and HgTe, and thus the numbers of defects more abundant that is usually expected. The completed defect calculations must allow for trigonal and tetrahedral distortions, which we are in the process of incorporating. This work will be presented at the HgCdTe conference in October.

At present our highest priority for the immediate future is to make the new electronic structure program, Section IV, run smoothly, and complete the crystal program. Once our new method can be applied, its potential for application is truly vast, and we are optimistic that it will become the most advanced of all electronic structure methods. After the basic algorithm is perfected, we will apply it to some of the problems mentioned in the earlier sections. The ones of greatest interest now are the completion of Schottky barrier studies, allowing full relaxation of atomic positions at the interface. Similarly, we will continue work already started in the low coverage regime. Defect studies now underway (this section) can also be studied with much greater facility.

In concert with the applications, we shall continue to elaborate on the method. The next steps are to incorporate the "iterative diagonalization" that makes the computation scale as the square of the number of atoms, and implementation on a parallel-processor machine, so as to make true dynamics containing many atoms a practical reality. All of this should be accomplished within the next year. This will allow us to make, for the first time, studies of larger scale defects such as grain boundaries in semiconductors, and complex reconstructions at semiconductor surfaces, and the evolution of these reconstructions as adatoms are deposited. This will tie in with exciting new development of experimental techniques that allow atomic-scale resolution of reconstructions at semiconductor interfaces.

Beyond this, we can incorporate the GW extension to LDA in this method, so as to eliminate the "bandgap" problem and make first-principles studies of optical properties feasible, such as defect levels in semiconductors.

Fig. 1. Product of 2 Hankel functions centered at A and B respectively (left). Approximation to product, expressed as a linear combination of Gaussian functions centered on A as in (1.1). Error in fit (right). By increasing the number of functions in the approximation, fit, and error can be made arbitrarily small.



[illegible] charge density of N_2 molecule (left). Superposition [illegible] free atomic ones [illegible] (bottom). Tendency to form a bond [illegible] evidenced by a [illegible] up of charge in the bond and a deficit of charge on the [illegible] of the molecule.

All densities shown are "smoothed" densities — exact in the interstitial, but approximate near the nuclei